

Patent claims

1. Organic solutions containing metal(IV) salts and oxoacids of phosphorus from which, after evaporation of the solvent, insoluble compounds of general composition $M(IV)(O_3P-G)_{2-n}(O_3P-R^1-X)_n$ can be obtained, where M(IV) is a tetravalent metal, -G is a generic inorganic or organic group, -R¹- is an organic group, -X is an acid group and n is a coefficient ranging from 0 to 1.5.
2. Organic solutions of claim 1 wherein the anion of the tetravalent metal salt is preferably chosen among carboxylates, chlorides and alkoxides.
3. Organic solutions of claim 1 or 2 wherein the tetravalent metal salt is preferably chosen between Zr, Ti, Sn and Ce or their mixture.
4. Organic solutions of any of claims 1-3 wherein the tetravalent salt is preferably the zirconyl propionate or chloride.
5. Organic solutions of any of the preceding claims wherein the group -G is preferably chosen among the acid groups -OH ; -R²-SO₃H and -R²-PO₃H₂, where -R²- is an organic group with preferably linear chain such as -(CH₂)_m- and -(CF₂)_m-.
6. Organic solutions of any of the preceding claims wherein the group -R¹- is an arylene group chosen preferably among -C₆H₄-; -C₆H₄-CH₂- and -C₆H₄-CF₂-.
7. Organic solutions of any of the preceding claims wherein the acid group -X is chosen between -SO₃H, -PO₃H₂ and -COOH.

8. Organic solutions of any of the preceding claims wherein the organic solvent is chosen among the protonable solvents, especially N,N-dimethylformamide, N-methyl-2-pyrrolidone, dioxane, dimethylsulfoxide, acetamide, acetonitrile, various alkanols and/or their mixtures, commonly used for dissolving the proton conducting ionomers of the state of art.
9. Use of the organic solutions of any of the preceding claims for the insertion of nano-particles of tetravalent metal salts, preferably phosphate-phosphonates, within the pores of polymeric or inorganic porous membranes.
10. A method for the filling of porous membranes of claim 9 with tetravalent metal salts, especially phosphate-phosphonates, based on the following steps:
- a) preparation of the organic solution of claims 1-8 which, at the same time, may also contain a polymer and/or an ionomer of the state of the art;
 - b) impregnation of the porous membrane with such a solution;
 - c) elimination of the solvent;
 - d) repetition of the steps b and c until the wished percentage of pore filling is obtained.
11. Proton conducting composite membranes made of polymeric or inorganic porous membranes with pores filled with tetravalent metal salts, especially phosphate-phosphonates, or mixtures of said compounds with a proton conducting ionomer and especially prepared by using the solutions of claims 1-8.
12. Proton conducting composite membranes of claim 11 wherein the polymeric porous membrane is preferably chosen between those made of chemically and/or thermally stable polymers, especially

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polytetrafluoroethylene (PTFE), polyvinylidene fluoride (PVDF), polyesters, polyethersulfones and fluoroelastomers.

13. Proton conducting composite membranes of any of claims 11 or 12
5 wherein the pore dimensions of the porous membranes are preferably in the range 0.02-20 μm , especially 0,1-10 μm , preferably 0,4-2 μm and the porosity >10 %, especially >50 %, preferably 65-90 %.
- 10 14. Proton conducting composite membranes of any of claims 11-13 wherein the tetravalent metal salts, preferably phosphate-phosphonates, for the filling of pores are chosen between $\text{Zr}(\text{O}_3\text{P}-\text{CH}_2-\text{PO}_3\text{H}_2)_2$ and compounds of the series $\text{Zr}(\text{O}_3\text{P}-\text{OH})_{2-n}(\text{O}_3\text{P}-\text{C}_6\text{H}_4-\text{SO}_3\text{H})_n$, and $\text{Zr}(\text{O}_3\text{P}-\text{C}_6\text{H}_4-\text{SO}_3\text{H})_{2-n}(\text{O}_3\text{P}-\text{CH}_2-\text{PO}_3\text{H}_2)_n$, with n
15 in the range 0.1-1.5.
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15. Composite membranes made up of a porous ceramic membrane partially filled with a tetravalent metal salt, preferably phosphate-phosphonate, according to one of claims 1-7 exhibiting catalytic
20 activity.
16. Composite membranes of claim 15 wherein the tetravalent metal salts, preferably phosphate-phosphonate, with catalytic activity is chosen among those reported in claim 14.
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17. Use of the organic solutions of any of claims 1-8 for the preparation of nano-polymers constituted by nano-particles of tetravalent metal salts, preferably phosphate-phosphonates, dispersed in the matrix of organic or inorganic polymers soluble in the same solvents.
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18. Use of the organic solutions of any of claims 1-8 for the preparation of nano-polymers of claim 17 wherein the organic polymeric matrix is that of a proton conducting ionomer.
- 5 19. A method for the preparation of nano-polymers and nano-ionomers of any of claims 17-18 based on:
- a) preparation of an organic solution having one of the compositions reported in the any of claims 1-8 and at the same time containing a polymer and/or an ionomer of the state of the art;
 - 10 b) elimination of the solvent.
20. The method for the preparation of nano-polymers and nano-ionomers of claim 19 wherein the elimination of the solvent is preferably performed by evaporation or with a non- solvent of the polymer or ionomer.
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21. Nano-polymers constituted by nano-particles of tetravalent metal salts, preferably phosphate-phosphonates, dispersed in the matrix of organic or inorganic polymers.
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22. Nano-polymers of claim 21 wherein the polymeric matrix is that of a synthetic ionomer of the state of the art preferably chosen among perfluorosulphonic polymers, sulfonated polyetherketones (sPEK), sulfonated polyethersulfones and sulfonated polyvinylidenefluoride (sPVDF).
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23. Nano-polymers of claims 21 or 22 wherein the nano-particles of tetravalent metal salts, preferably phosphate-phosphonates, dispersed in the polymeric matrix are chosen among those exhibiting proton conductivity $> 10^{-2} \text{ S cm}^{-1}$ at 70 °C and 95 % relative humidity.
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24. Nano-polymers of any of claims 21-23 wherein the nano-particles of tetravalent metal salts, preferably phosphate-phosphonates, are those constituted by the same compounds of claim 14.
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25. Use of the organic solutions of any of claims 1-8 for the preparation of membranes constituted by nano-polymers of claims 21-24.
26. Nano-ionomeric proton conducting membranes constituted by nano-polymers of any of claims 21-25.
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27. Use of the organic solutions of any of claims 1-8 for an easy insertion of a large variety of lamellar nano-particles of tetravalent metal salts, preferably phosphate-phosphonates, in the membrane/electrode interfaces of PEM FCs.
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28. Use of the organic solutions of any of claims 1-8, with the addition of ionomers and/or other proton conducting compounds soluble in the same solvents, for an easy insertion of a large variety of lamellar nano-particles of tetravalent metal salts, preferably phosphate-phosphonates, in mixture with other proton conducting compounds in the membrane/electrode interfaces of PEM FCs.
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29. Use of proton conducting membranes constituted by inorganic or polymeric porous membranes with pores filled with tetravalent metal salts, preferably phosphate-phosphonates, of any of claims 11-16 and of membranes constituted by nano-polymers of claim 26, in electrochemical devices.
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30. Use of proton conducting membranes of claim 29 in electrochemical devices specifically planned for generating electrical energy from the oxidation of a fuel.
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31. Use of proton conducting membranes of claim 29 in fuel cells specifically planned for electrical vehicles and/or for portable electrical devices.
- 5 32. Use of composite membranes of claim 29 for improving the global performance of ionomeric membranes of the state of the art in hydrogen, indirect methanol and direct methanol fuel cells.
- 10 33. Use of membranes of claim 11, 15 and 16 in catalytic membrane reactors.
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